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Laser Synthesis of Transitional Metal Oxides in 2D Structure and Heterostructure for Thermo Sensors with High Seebeck Coefficient

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Abstract

Ultraviolet photons of KrF-laser (λ = 248 nm) based on reactive pulsed laser deposition (RPLD) were used for the synthesis of chromium oxides ($Cr_{3-X}O_{3-Y}$), iron oxides (Fe_2O_{3-X}) 2D structures and $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D heterostructure with variable stoichiometry, electrical properties and thickness. 2D structures' depositions were carried out on <100>Si substrate at its temperature change in the range of 293-800 K. XRD analysis showed the evidence of these structures deposited on substrate had polycrystalline phases' content. All 2D structures and heterostructures demonstrated semiconductor temperature behaviour with variable band gap (E_g) less than 1.0 eV, depending on substrate temperature, oxygen pressure in the reactor and structure thickness. Thickness of all kinds' deposits (55-75 nm) depended on oxygen pressure, substrate temperature and the number of laser pulses. The optimum oxygen pressure and substrate temperature were found when thermo electromotive force coefficient (Seebeck coefficient, S) was high as 3.0-8.0 mV/K for $Cr_{3-X}O_{3-Y}$ and for Fe_2O_{3-X} 2D structures, accordingly, in the range (280-330) K. The highest S coefficient obtained for 4 layered $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D heterostructures was about 15 mV/K in the range (280-330) K. This made these 2D structures and 2D heterostructures, synthesized by UV photons using RPLD method, an exceptionally strong candidate for effective thermo sensors operating at moderate temperature.

Keywords

Laser Deposition; 2D Structures; 2D Heterostructures; Oxides; Thermo Sensors

Introduction

Effective thermoelectric materials are characterized with high thermo electromotive force coefficient (Seebeck coefficient, S) and high thermoelectric figure of merit (ZT). These properties make them quite effective materials for modern electronic devices, namely, thermo sensors and thermo converters. The most effective materials for this propose are semiconductor materials with 2D dimensional size based on transitional metal oxides. These nanometric materials in the form of thin films (i.e. 2D dimensional) with accurately tailored band gap are actively studied not only to their semiconductor properties, but electrochromic and photochromic properties too [Hussain, 2001, Mulenko et al. 2006]. Most of their properties depend on the band gap value, which in turn depends on the oxide structure stoichiometry and thickness. Our interest is the deposition of $Cr_{3-X}O_{3-Y}$ ($0\leq x\leq 2$; $0\leq y\leq 2$), Fe_2O_{3-X}($0\leq x\leq 1$) 2D structures and $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D heterostructure on <100> Si substrate with variable stoichiometry variable band gap and to test their thermoelectric properties. To this end, we used the reactive pulsed laser deposition (RPLD) technique as it is quite simple and fast process with using elemental target and low-pressure gases in the reactor. RPLD allows a good control of structure thickness with varying the number of laser pulses (N) and stoichiometry of deposits with varying the gas pressure in the deposition reactor too.

Chromium oxide 2D structures were deposited before with high S coefficient by RPLD at room temperature (RT) Si substrate [Caricato et al. 2010; Mulenko. 2011]. Iron oxide 2D structures with the S $\cong$ 1.6 mV/K were deposited before [Mulenko et al. 2011]. But the highest S coefficient for Fe_2O_{3-X} 2D structure as high as 3-8 mV/K in the range

of 280-330 K was obtained while deposition on heated Si substrate with RPLD [Mulenko et al, 2014]. The highest S coefficient for $Cr_{3-X}O_{3-Y}$ 2D structure as high as 3-8 mV/K in the range 240-330 K was obtained while deposition on heated Si substrate [Mulenko et al. 2014]. Nevertheless, it further remains very important problem to increase the S coefficient as much as possible. Here we propose to increase the S coefficient with using not only Fe_2O_{3-X} and $Cr_{3-X}O_{3-Y}$ 2D structure, but $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D heterostructure. Therefore, it is very important to investigate the influence of crystallization process and structure heterogeneity on thermoelectric properties (i.e. Seebeck coefficient). Nanometric $Cr_{3-X}O_{3-Y}$, Fe_2O_{3-X} and $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D heterostructure were investigated as their application for thermo sensor with high S coefficient.

There are some works to have been carried out by other investigators devoted to measuring of the S coefficient based on other materials. For an example, the S coefficient was about 0.85 mV/K in two-dimensional electron gas for $SrTiO_3$ [Ohta et al. 2007]. Oxide thermoelectric material as *p*-type $Ca_3Co_4O_9$ semiconductor in the form of epitaxial thin films and polycrystalline ceramic the S coefficient was about 0.2 mV/K at 1000 K [Ohta et al. 2008]. Sr-Ru-O powders were synthesized by spark plasma sintering in solid state reaction [Keawprak et al. 2008]. Polycrystalline Sr_2RuO_4 powder exhibited semiconductor behaviour from RT to 1000 K. The highest positive Seebeck coefficient for polycrystalline Sr_2RuO_4 powders synthesized by this method was about 0.042 mV/K at 600 K. Negative S coefficient (-0.4 mV/K) was obtained for PbSe and PbTe bulk [Ishida et al. 2009]. It should be mentioned that all these materials have not so high S coefficient. Moreover, these materials were synthesized using toxic atoms such as Te, Sb, Se, Pb, and Sr. Therefore, there is the problem to obtain thermoelectric material with high S coefficient operating at moderate temperature without using toxic precursors as a background of "green technologies". The RPLD technique is used, where a pure chromium and iron targets were ablated by energetic KrF laser (λ = 248 nm) pulses in low pressure O_2 atmosphere ($\leq$1.0 Pa) to synthesize $Cr_{3-X}O_{3-Y}$ 2D, Fe_2O_{3-X} 2D structures and $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D heterostructure. The results of high Seebeck coefficient at moderate temperature (280-330 K) obtained on the base of these 2D structures and 2D heterostructures synthesized by RPLD are presented and discussed in this paper. Moreover, the comparison of electrical, structural and thermo sensor properties for these structures and heterostructures was carried out this paper too.

Experimental

Laser Deposition of 2D Structures and 2D Heterostructures

Structures' depositions were carried out in a stainless-steel vacuum reactor. Before each deposition, the reactor was evacuated down to a residual pressure of ~ 4.5×10^{-5} Pa to avoid contamination. Then, the flux of pure O_2 (99.999%) was introduced and stabilised to the desired dynamic pressure in the range of (0.1-1.0) Pa. A pure Fe (99.5%) and Cr (99.5%) targets were ablated with a KrF (λ = 248 nm) laser pulses at a fluence of 4.0 J/cm^2 and frequency repetition rate of 10 Hz. The duration of the pulse was ~ 25 ns. Each 2D structure and 2D multilayer heterostructure was deposited on high resistance <100>Si substrate by a definite number of laser pulses (N), namely 1000 – 5000 at definite oxygen pressure in the reactor. The Cr and Fe targets were rotated at a frequency of 3 Hz to avoid piercing and ensure a smooth ablation procedure. Before each deposition, the target surface was cleaned by 3000 laser pulses with a shutter shielding the substrate. Substrates were parallel at 45-mm distance from Fe and Cr targets and cleaned before in an ultrasonic bath with acetone, ethylic alcohol and finally rinsed in deionised water. The flux of ablated Fe or Cr atoms from their targets at definite oxygen pressure was deposited on RT or heated Si substrate to the synthesis of Fe_2O_{3-X} or $Cr_{3-X}O_{3-Y}$ 2D structures. As regards to $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D heterostructure, the corresponding fluxes of ablated Fe or Cr atoms, respectively at definite oxygen pressure were deposited step by step on RT or heated Si substrate to the synthesis of 2D multilayer heterostructures.

Measurements of Thermo Sensor Properties of 2D Structures and 2D Heterostructures

The thickness of deposited 2D structures and 2D heterostructures was measured by "Tensor Instruments" model "Alpha-step 100" profilemeter with an error of 5 %. The crystalline structure of deposited 2D structures and 2D heterostructures studied with X-ray diffractometer (XRD) STADI "Stoe" at 45 kV and 33 mA (Cu K_α radiation). The direct current (DC) electrical resistance of the deposited 2D structures and 2D heterostructures was measured by two-probe technique. Ohmic contacts were obtained by silver paste coatings. Temperature dependences of the electrical resistance of the deposited, these structures were measured with a high resistance multimeter.

Heterostructure from electrical point of view is an analogous of parallel connection of some electrical resistance where single layer is a resistance in parallel connection. Therefore, 2D heterostructure can be characterized with an equivalent specific conductivity (σ). Calculations of an equivalent specific conductivity of the deposited 2D multilayer heterostructure were performed taking into account of this heterostructure thickness (d) and the geometrical shape of Si substrates with the deposits (0.8x0.25) cm^2. Special installation was used for temperature measurement of a sample and temperature difference (ΔT) between heated and room temperature (RT) end or cooled and RT end of a sample. These measurements were carried out by using two thermocouples attached to 2D structures with high thermo conductivity clue (1-2, 2-1). Principal measurement scheme of thermo sensor is shown in Fig.1.

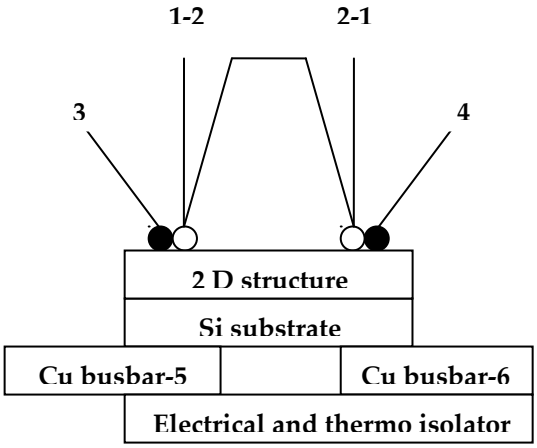

FIG. 1 THE MEASUREMENT SCHEME OF 2D STRUCTURE AND 2D HETEROSTRUCTURE OF THERMO SENSOR (NOT TO SCALE)

The thermo e.m.f. (ΔV) was measured (contacts 3-4) between heated or cooled Cu busbar-5 and RT Cu basbar-6. The temperature dependence of the S coefficient was measured from these data as a ratio of $\Delta V/\Delta T$ in the range of 230-330 K after producing a thermal gradient along the sample (ΔT).

Results and Discussions

Electrical and Structural Properties of Deposited 2D Structures and 2D Heterostructures

The temperature dependence of $Cr_{3-X}O_{3-Y}$, Fe_2O_{3-X} 2D structures and $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D multilayer heterostructures for σ demonstrated the typical behaviours of semiconductor materials which could be described by the well-known expression [Wert et al.1964]:

$$\sigma = \sigma_g \exp(-E_g/2kT) + \sigma_i \exp(-E_i/kT), \quad (1)$$

where σ_g is the intrinsic conductivity for 2D structure or 2D multilayer heterostructure; σ_i is the conductivity for 2D structures or 2D multilayer heterostructure determined by impurities; k is the Boltzmann constant; E_g is energy band gap for the intrinsic conductivity of 2D structures or 2D multilayer heterostructure and E_i is energy band gap for these structures assigned to impurities in the iron oxides and chromium oxides (e.g. unreacted iron and chromium atoms). In our experimental conditions when T > RT, the intrinsic conductivity for 2D structure or 2D multilayer heterostructure (σ_g) is governed by the main intrinsic charge carriers. Therefore, it is possible to calculate E_g from the following expression:

$$E_g = \frac{2k \ln[\sigma(T_1)/\sigma(T_2)]}{1/T_2 - 1/T_1}, \quad (2)$$

where $\sigma(T_1)$ and $\sigma(T_2)$ are the intrinsic conductivity for 2D structure or 2D multilayer heterostructure at the temperature T_1 and T_2, accordingly, when $T_1 > T_2$. The temperature dependences of the specific conductivities of the deposited 2D structure and 2D multilayer heterostructures were measured in the range of 280-330 K to test the semiconductor behaviour of these deposits. An equivalent band gaps were calculated with uncertainty about 10%. The optimum conditions were found, including oxygen pressure (PO_2) in the reactor, substrate temperature (T_S), structure thickness (d) for the highest S coefficient. Temperature dependencies of the specific conductivity of Cr_{3-}

$_xO_{3-Y}$ 2D structure at PO_2=0.5 Pa, as optimum pressure, are shown in Fig.2. Chromium oxides' 2D structure thickness at this pressure is being increased from 55 nm to 70 nm while Si substrate temperature (T_S) enlarge from 293 K to 800 K. Taking into account of geometrical shape of deposited $Cr_{3-x}O_{3-Y}$, 2D structure and its thickness, σ were calculated (Fig.2).

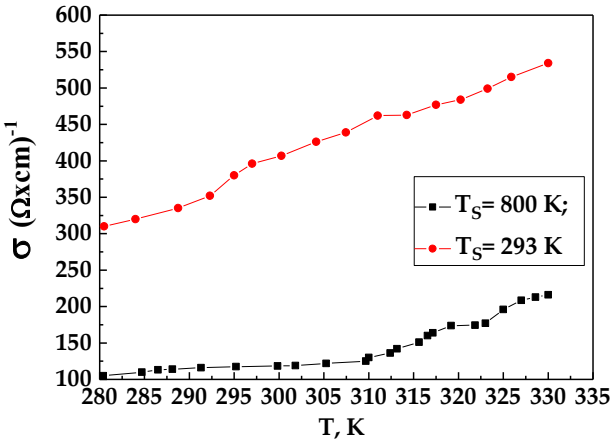

FIG. 2 TEMPERATURE DEPENDENCIES OF CHROMIUM OXIDES SPECIFIC CONDUCTIVIYU 2D STRUCTURE DEPOSITED AT PO_2 = 0.5 Pa AND DIFFERENT SUBSTRATE TEMPERATURE

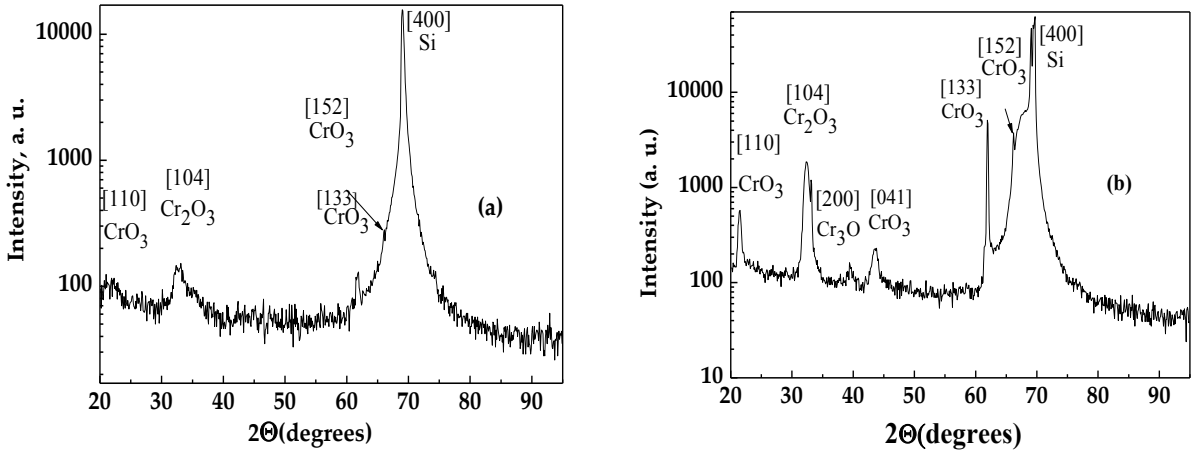

FIG. 3 XRD DIAGRAM OF CHROMIUM OXIDE 2D STRUCTURE AT PO_2=0.5 Pa AND DIFFERENT SUBSTRATE TEMPERATURE: **a** -T_S = 293 K, **b**-T_S = 800 K

Taking into account of the expression (2), E_g was evaluated for each 2D structure and 2D heterostructure too. Value of the S coefficient strongly depends on E_g to be assigned with oxides' phases content. Therefore, it is very important to have structural content of deposits. XRD analysis gave the information about phase content of synthesized $Cr_{3-x}O_{3-Y}$, Fe_2O_{3-x} 2D structures and $Fe_2O_{3-x}/Cr_{3-x}O_{3-Y}$ 2D heterostructure (Figs.3, 5, 7). While $Cr_{3-x}O_{3-Y}$ 2D structure deposition on 293 K and 800 K substrate, E_g is being increased from 0.15 eV to 0.47 eV owing to increasing chromium oxides' phases content with higher E_g values. Oxygen contribution in the deposited of these structures comes out from homogeneous and heterogeneous reactions between chromium atoms and oxygen molecules in the volume above substrate surface and on its surface during film growth. XRD diagrams confirm that semiconductor structures consist of chromium atoms with different degrees of oxidation resulting in different value of E_g. Semiconductor properties of the deposited structures should be assigned with crystalline semiconductor CrO_3 and Cr_2O_3 phases' content (Fig.3a, b). As it is known, chromium atoms are in different oxidation degrees in these semiconductor phases (i.e. 6 and 3 oxidation degree of Cr atoms). As it is seen from XRD analysis, there is different concentration of these semiconductor phases. It should be taken into account that each semiconductor phase has its own Eg value. Equivalent total Eg of oxides' mixture with different Eg depends on concentration of each

semiconductor phase synthesized at definite conditions (e. g. oxygen pressure, substrate temperature, structure thickness).

Temperature dependencies of the specific conductivity of Fe_2O_{3-X} 2D structure deposition at PO_2=0.5 Pa on 293 K and 800 K substrate are presented in Fig.4. E_g is being decreased from 0.86 eV to 0.32 eV owing to iron oxides' phases increasing with lower E_g values. And while increasing substrate temperature from T_S=293 K to T_S=800 K at PO_2=0.5 Pa, Fe_2O_{3-X} 2D structure thickness is being increased from 26 to 36 nm. XRD diagrams confirm that semiconductor films consist of iron atoms with the same degrees of oxidation depending on substrate temperature resulting in different value of E_g. The more substrate temperature is, the more iron oxides' phases are in synthesized Fe_2O_{3-X} 2D structure (Fig.5). Iron oxides phases' concentrations with lower Eg are being increased with the increasing temperature of Fe_2O_{3-X} 2D structure. Equivalent total Eg of oxides' mixture with different E_g depends on concentration of each semiconductor phase synthesized at definite conditions too (e.g. oxygen pressure, substrate temperature, structure thickness).

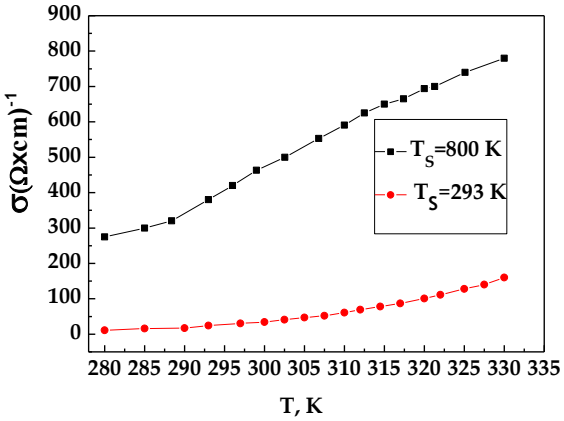

FIG. 4 TEMPERATURE DEPENDENCIES OF IRON OXIDES SPECIFIC CONDUCTIVITY 2D STRUCTURE DEPOSITED AT PO_2 = 0.5 Pa AND DIFFERENT SUBSTRATE TEMPERATURE

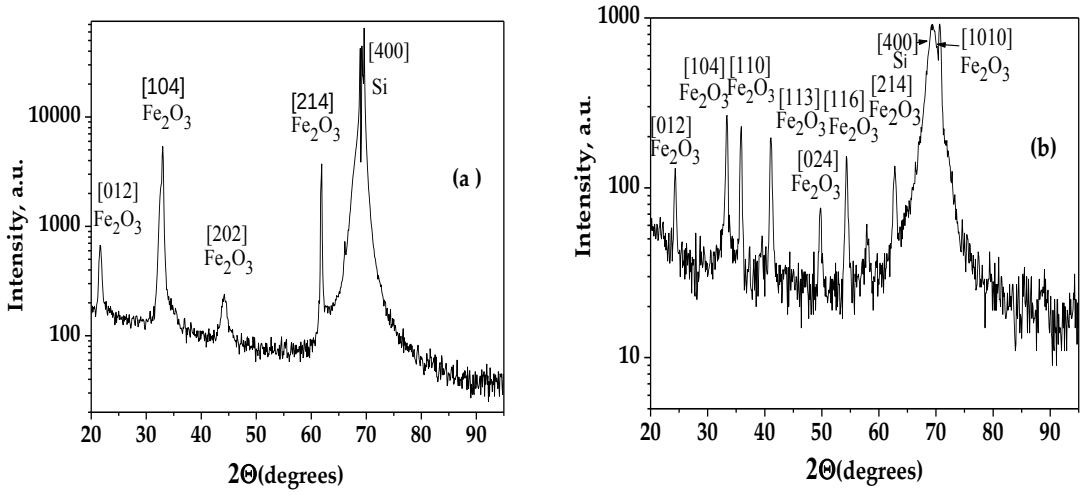

FIG. 5 XRD DIAGRAM OF IRON OXIDE 2D STRUCTURE AT PO_2=0.5 Pa AND DIFFERENT SUBSTRATE TEMPERATURE: **a**-T_S =293 K, **b** - T_S =800 K.

In general, the increase of oxygen pressure in the reactor resulted in decreasing oxides' lines due to the decrease of crystalline status in deposited structures, as the increase of oxygen pressure caused a kinetic energy loss of iron atoms and their ions owing to increasing of collision frequency with oxygen molecules [Mulenko et al. 2014]. Correspondingly, the cooling time of structures on a substrate decreases and the crystallization status is worsening. On the other hand, in the case of substrates temperature of 800 K, the number of the iron oxide lines in XRD

diagram are enhanced (Fig.5), as the kinetic energy of iron atoms, their ions and cooling time are increased resulting in the growth of a more amount of Fe_2O_{3-X} semiconductor phases in the deposited structures [Mulenko et al. 2014]. The substrate temperature increases resulting in the increasing of σ value owing to higher crystalline phases' content. So the more substrate temperature is, the more new iron oxide phases appear in the deposited structures owing to kinetic energy increasing for the formation of these new phases in the comparison with 293 K substrate temperature (Fig.5). Many different types of $Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}$ 2D multilayer heterostructure (i.e. 2D multilayer heterostructure deposited at different T_S, PO_2 and different number of layers: 2-8 layers) were investigated to find out the optimum conditions to obtain these heterostructures with the highest S coefficient. Temperature dependences of an equivalent specific conductivity of $Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}$ 2D multilayer heterostructures (4 layers) were investigated while deposition on Si substrates at its temperature 293, 600 and 800 K in order to find out the equivalent band gap influence on the S coefficient (Fig.6).

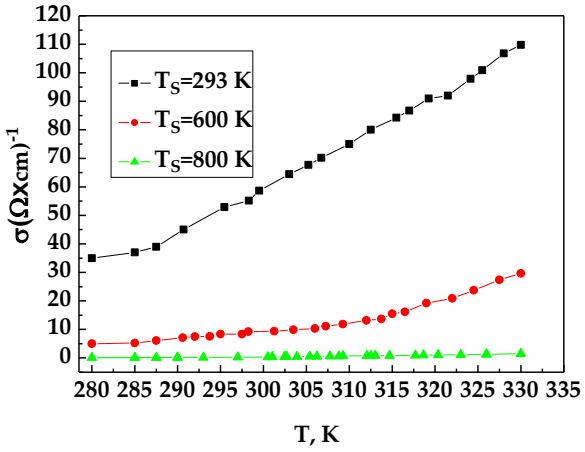

FIG. 6 TEMPERATURE DEPENDENCIES OF AN EQUIVALENT SPECIFIC CONDUCTIVITY OF $Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}$ 2D MULTILAYER HETEROSTRUCTURE DEPOSITED AT PO_2 = 0.5 Pa AND DIFFERENT SUBSTRATE TEMPERATURE

As it is seen from temperature dependences of an equivalent specific conductivity, 2D multilayer heterostructure deposited on Si substrate at T_S =293, 600 and 800 K, they demonstrated typical semiconductor trends (Fig.6). The equivalent band gap of $Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}$ 2D multilayer heterostructures is being increased with increasing substrate temperature while structure deposition. Namely, when substrate temperate is 293, 600 and 800 K, E_g is 0.36, 0.57 and 0.87 eV, accordingly. 2D heterostructure thickness is being increased from 65 nm to 75 nm with T_S increasing from 293 K to 800 K. Phase content of $Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}$ 2D multilayer heterostructures (4 layers) was investigated too (Fig.7).

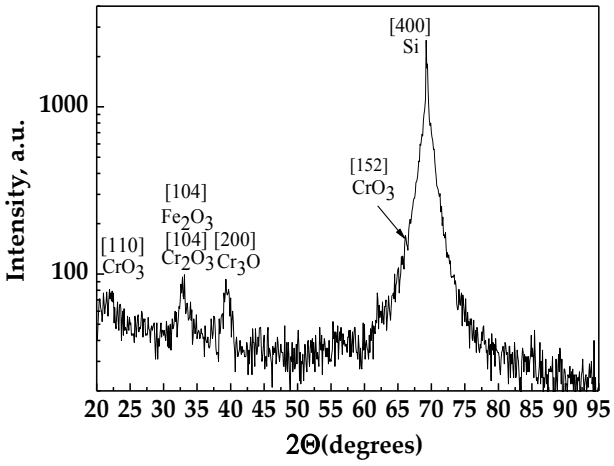

FIG. 7 XRD DIAGRAM OF $Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}$ 2D MULTILAYER HETEROSTRUCTURE DEPOSITED AT PO_2 = 0.5 Pa AND T_S = 800 K

As it is seen from Fig.7, the intensities assigned with chromium oxides' and iron oxides' peaks are sufficient lower and diffused for deposited $Cr_{3-x}O_{3-y}/Fe_2O_{3-x}$ 2D multilayer heterostructure in comparison with single these oxides' 2D structures, as iron and chromium oxides are partly converted into amorphous chromite ($FeCr_2O_4$). As it is known, polycrystalline chromite ($FeCr_2O_4$) can be synthesized from powder of pure FeO and Cr_2O_3 at 1673 K [Wang et al. 2015]. But in our experiment, the highest temperature for $Cr_{3-x}O_{3-y}/Fe_2O_{3-x}$ 2D multilayer heterostructure was 800K. This temperature is sufficiently lower than 1673 K. Therefore, there is no polycrystalline chromite with the following stoichiometry: Fe:Cr:O=1:2:4 in layers' interface.

Thermo Sensor Properties of Deposited 2D Structures and 2D Heterostructures

Measurement method of the S coefficient is such as the uncertainty in determining of its value which is no more than 2% in the temperature range of 310≤T≤290 K. But this method demonstrates uncertainty about 10% in determining the S coefficient in the temperature range of 290≤T≤310 K, as an error in a measurement of temperature difference in this range is sufficiently higher than in the temperature range of 310≤T≤290 K. These measurements of the S coefficient were carried out no less than for three samples with identical structure. Identical structure is the structure deposited at the same oxygen pressure, substrate temperature and number of laser pulses.

Thermo electromotive force coefficient of $Cr_{3-x}O_{3-y}$ 2D structure deposited by RPLD on Si substrate versus its temperature at PO_2 = 0.5 Pa inside the reactor and different substrate temperature is shown in Fig.8.

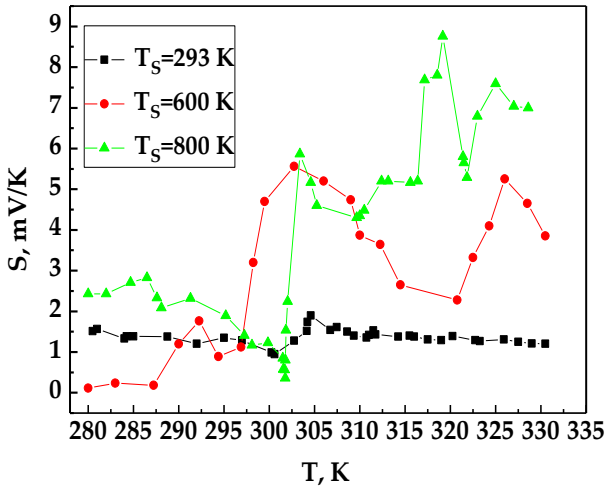

FIG. 8 THERMO ELECTROMOTIVE FORCE COEFFICIENT VS. TEMPERATURE OF $Cr_{3-x}O_{3-y}$ 2D STRUCTURE DEPOSITED AT PO_2 = 0.5Pa AND AT DIFFERENT SUBSTRATE TEMPERATURE.

Substrate temperature (T_S) increasing up to 800 K results in the increasing of crystalline semiconductor CrO_3 and Cr_2O_3 phases' content, and therefore results in increasing of the S coefficient in the deposited 2D structure (Fig.8). One can explain this phases' content increasing by the rate constant increasing of chemical reaction upon gas pressure and the reaction temperature. Namely, oxygen pressure 0.5 Pa and the increasing substrate temperature up to 800 K are the conditions for increasing CrO_3 and Cr_2O_3 phases' content in the deposited 2D structure owing to the rate constant increasing of chemical reaction between Cr atoms and O_2 molecules with temperature increasing. Therefore, substrate temperature increasing at these conditions results in the increasing of the S coefficient in the range 300-330 K.

The S coefficient of Fe_2O_{3-x} 2D structure deposited by RPLD on Si substrate versus its temperature at PO_2 = 0.5 Pa inside the reactor and different substrate temperature is presented in Fig.9. Substrate temperature (T_S) increasing up to 800 K results in increasing of crystalline semiconductor Fe_2O_3 phases' content, and therefore results in the increasing of the S coefficient in the deposited 2D structure (Fig.9). One can explain this phases' content increasing by the rate constant increasing of chemical reaction between Fe atoms and O_2 molecules upon gas pressure and the reaction temperature. Namely, oxygen pressure 0.5 Pa and the increasing substrate temperature up to 800 K are the conditions for increasing Fe_2O_3 phases' content in the deposited 2D structure.

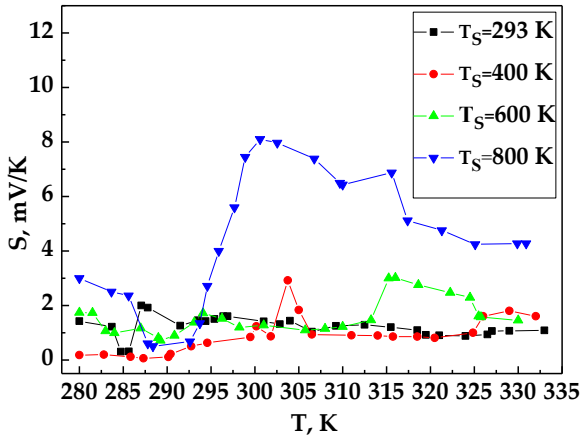

FIG.9 THERMO ELECTROMOTIVE FORCE COEFFICIENT VS. TEMPERATURE OF Fe_2O_{3-X} 2D STRUCTURE DEPOSITED AT PO_2 = 0.5Pa AND AT DIFFERENT SUBSTRATE TEMPERATURE.

Thermo e.m.f. coefficient of $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$2D multilayer heterostructure deposited by RPLD on Si substrate versus its temperature at PO_2 = 0.5 Pa inside the reactor at different substrate temperature (T_S) while heterostructure deposition was investigated too (Fig.10). Substrate temperature increasing up to 800 K results in decreasing of crystalline semiconductor CrO_3, Cr_2O_3, Fe_2O_3 phases' content (Fig.7). But in this case the S coefficient of the deposited 2D multilayer heterostructure is being increased (Fig.10). The S coefficient is more uniform in comparison with Fe_2O_{3-X} or $Cr_{3-X}O_{3-Y}$ 2D single layer structure. Such behaviours can be explained with no so sharp oscillation of effective density-of-states in the conduction and valence bands owing to the increasing of effective density-of-states as the result of overlapping electron states of each kind layer in 2D multilayer heterostructure. In general, increasing of an effective density-of-states results in S coefficient increasing.

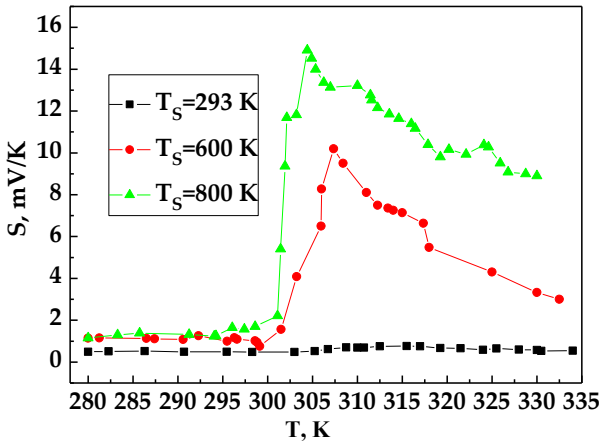

FIG. 10 THERMO ELECTROMOTIVE FORCE COEFFICIENT VS. TEMPERATURE OF $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D MULTILAYER HETEROSTRUCTURE DEPOSITED AT PO_2 = 0.5Pa AND AT DIFFERENT SUBSTRATE TEMPERATURE.

As it is known, the S coefficient is an important factor for studying kinetic phenomena of charge transfer in materials [Nalwa. 2000]. To this purpose, it is necessary to know besides the correlation between the temperature and the specific conductivity, the correlation between the temperature and the S coefficient should be studied. If one takes into account of the expressions for electron and hole concentrations in a non-degenerate semiconductor, it is possible to express the S coefficient in the following form [Shalimova. 1985]:

$$S = -\frac{k}{e}\left\{\frac{[2+\ln(N_c/n)]n\mu_n - [2+\ln(N_v/p)]p\mu_p}{n\mu_n + p\mu_p}\right\}, \quad (3)$$

where k is the Boltzmann constant; e is electron charge; n, p are electron and hole concentrations, respectively; N_c,

N_v are effective density-of-states in the conduction and valence bands, respectively; and μ_n, μ_p are electron and hole mobility, respectively. It is seen that the S. coefficient of semiconductor materials is determined with carriers of two parts: electrons and holes (3). The S coefficient has different maximum values for various films deposited on Si substrates and it varies with substrate temperature (Figs. 8, 9). This non-uniform variation of the S coefficient of the deposited films can be explained by an oscillation of effective density-of-states for valance and conductive bands and for impurity levels too. Namely, while temperature changes in the comparison with the sample end at RT, there is local changing of charge carriers' concentration (i.e. existence concentration gradient) resulting in the appearance of the thermo e.m.f. force between two sample ends. As it is seen, the S coefficient is positive in all measured temperature range because *p*-type carriers prevail above *n*-type once in all 2D structures and 2D heterostructures (Figs.8-10). As it is known, there are quantum dimensional effects in 2D semiconductor structure with narrow band gap [Kiselev et al. 1999]. It is followed from quasi-pulse periodic Karman-Born conditions where effective density of N_c and N_v states in two dimensional zone is proportional to effective mass of free charge carriers and equal for substrate surface unit

$$N_S = \frac{m_p^*}{h^2}, \tag{4}$$

where m_p^* is effective mass of free charge carriers in 2D structure or 2D heterostructure plate; *h* is Plank constant. Effective density of N_c and N_v states in two dimensional zone evaluated for 2D structure volume unit is the following:

$$N_V = \frac{m_p^*}{h^2 d}, \tag{5}$$

where d is 2D structure or 2D heterostructure thickness. N_c and N_v oscillations occur owing to effective mass change of free charge carriers while the change of 2D structure temperature [Frederiks et al. 1964]. As it is seen from the expression (5), the less 2D structure or 2D heterostructure thickness is, the more effective density-of-states in the conduction and valence bands will result in the increasing of the S coefficient. Increasing of charge carriers' concentration is not constant with increasing substrate temperature as there is the saturation of these concentrations on the states for valance and conductive bands and for impurity levels at definite temperature difference. Additional increasing temperature is a reason of additional increasing of charge carriers' concentration owing to their transition on higher energy levels at higher temperature. This oscillation is being appeared during sample heating. Such oscillation is more sufficient for Fe_2O_{3-X} or $Cr_{3-X}O_{3-Y}$ 2D single layer structure than for $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D multilayer heterostructure owing to less effective density-of-states (N_c and N_v) for single layer structures than for multilayer heterostructure. The optimum conditions at which the S coefficient was the highest as for 2D single layer structures and for 2D multilayer heterostructures were found out (i.e. PO_2=0.5 Pa and T_S=800 K). All parameters for 2D single layer structures and 2D multilayer heterostructures deposited with RPLD in different conditions are summarised and presented in Table 1.

TABLE 1 PARAMETES OF $CR_{3-X}O_{3-Y}$, FE_2O_{3-X} 2D SINGLE LAYER STRUCTURES AND $FE_2O_{3-X}/CR_{3-X}O_{3-Y}$ 2D MULTILAYER HETEROSTRUCTURES DEPOSITED WITH RPLD ON <100>SI SUBSTRATE AT OXYGEN PRESSURE OF 0.5 PA IN THE REACTOR AND DIFFERENT SUBSTRATE TEMPERATURE

2D Single Layer Structures and 2D Multilayer Heterostructures	Film Thickness d (nm)	Substrate Temperature T_S (K)	Energy Band Gap E_g (eV)	Seebek Coefficient S_{max} (mV/K) in the Range (280-330) K
$Cr_{3-X}O_{3-Y}$	55	293	0.15	3.0
$Cr_{3-X}O_{3-Y}$	70	800	0.47	8.0
Fe_2O_{3-X}	26	293	0,86	3.0
Fe_2O_{3-X}	36	800	0.32	8.0
$Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}/Cr_{3-X}O_{3-y}/Fe_2O_{3-X}/ Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}/ Cr_{3-X}O_{3-Y}/ Fe_2O_{3-X}$	65	293	0.36	1.0
$Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}/ Cr_{3-X}O_{3-Y}/Fe_2O_{3-X}/ Cr_{3-X}O_{3-Y}/ Fe_2O_{3-X}$	75	800	0,87	15.0

Conclusions

The thermoelectric properties of polycrystalline Fe_2O_{3-X}, $Cr_{3-X}O_{3-Y}$ 2D single layer structures and $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D multilayer heterostructures deposited by RPLD using a KrF-laser (λ = 248 nm) were investigated for the first time in the temperature range 280-330 K. It was shown that thermo e.m.f. coefficient (Seebeck coefficient, S) strongly depends on electrical and structural properties of deposited these 2D structures and 2D heterostructures. The presented results show that RPLD can be used to produce of polycrystalline 2D structures and 2D heteristructures based on iron and chromium oxides with variable thickness, variable degree of atoms' oxidation and variable band gap resulting in variable S coefficient. The optimum conditions (i.e. oxygen pressure in the reactor, substrate temperature, 2D structure's and 2D heterostructure's thicknesses) for the highest value of the S coefficient were identified. These values are essentially higher in comparison with other bulk or 2D structures thermoelectric materials. Thermo e.m.f. coefficient was high as 3.0-8.0 mV/K for $Cr_{3-X}O_{3-Y}$ and for Fe_2O_{3-X} 2D single layer structures, accordingly in the range of (280-330) K. The highest S coefficient obtained for $Fe_2O_{3-X}/Cr_{3-X}O_{3-Y}$ 2D multilayer heterostructures was about 15 mV/K in the range of (280-330) K. Nature and reason of such high obtained values of the S coefficient were explained. Non-toxic atoms and molecules are used in the proposed technology in comparison with other technologies based on using toxic precursors. It should be concluded that 2D structures and 2D heterostructures, synthesized by UV photons, using RPLD method, which is based on non-toxic precursors, are advanced materials with high Seebeck coefficient for effective thermo sensors operating at moderate temperature. These kinds of 2D structures and 2D heterostructures can be used as thermo sensors in bioelectronics to determine the thermal effect of chemical reactions.

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